was collected and recrystallized several times from ethyl acetate from which solvent it was obtained in clusters of needles melting at 186°.

Anal. Calcd. for $C_{27}H_{26}ClN$: Cl, 8.89. Found: Cl, 8.94.

The free base from the above hydrochloride crystallizes from ligroin in colorless, prismatic plates, m. p. 61–62°.

Anal. Calcd. for $C_{27}H_{25}N$: N, 3.86. Found: N, 3.78.

This substance is a primary amine and the results of analysis of itself and its derivatives agree with its formulation as an aminotribenzylbenzene. Hofmann, in his study of the molecular rearrangement of phenyltrimethylammonium iodide, obtained mesidine.[6] By analogy it is probable that the above aminotribenzylbenzene is 1-amino-2,4,6-tribenzylbenzene.

Benzoylaminotribenzylbenzene.—This compound crystallizes from alcohol in needles, m. p. 149°. *Anal.* Calcd. for $C_{34}H_{29}ON$: N, 3.00. Found: N, 3.01.

Tribenzylbenzene-azo-β-naphthol.—Crystallizes from alcohol in scarlet prisms with copper glance, m. p. 146°. *Anal.* Calcd. for $C_{37}H_{30}ON_2$: N, 5.41. Found: N, 5.61.

Summary

The molecular rearrangement of dibenzylaniline hydrochloride has been studied. The rearrangement proceeded at a comparatively low temperature with formation of *p*-aminodiphenylmethane, 1-amino-2,4-dibenzylbenzene and a third amine which is probably 1-amino-2,4,6-tribenzylbenzene. This would appear to be the first instance where three migrating groups have been introduced into the aniline ring during the rearrangement of a secondary or tertiary aniline base.

CORK, IRELAND RECEIVED NOVEMBER 29, 1939

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(6) Hofmann, *Ber.*, **5**, 715 (1872).

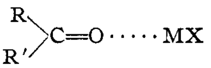
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Coördinate Compounds in the Color Test for Organometallic Compounds[1]

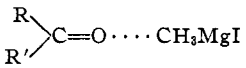
BY HENRY GILMAN AND R. G. JONES

The color test[2] is probably the most useful laboratory tool in studies on organometallic compounds. However, because Michler ketone, the essential compound in the color test, can form coördinate compounds with Grignard reagents, it is necessary to examine the possible interference effects of coördinate compounds.

The formal relationship of organometallic compounds to salts, made it a relatively short step from Werner's[3] coördination structures of the carbonyl type with salts [A], to the suggestion, which probably first was proposed by Straus,[4] for coördination compounds of ketones with the



[A]



[B]

Grignard reagent [B]. Later, v. Braun[5] and then, particularly, Meisenheimer and co-workers[6] and Hess and Rheinboldt[7] used the coördination structures as a basis for interpreting some reactions of carbonyl compounds with the Grignard reagent.[8]

There is no doubt that coördination complexes of some sort are formed with many ketones and Grignard reagents. Not only have some of the complexes been isolated and analyzed, but they have been hydrolyzed to the original ketones.[9] The most interesting and suggestive recent study is by Pfeiffer and Blank.[10] They examined the molecular compounds derived by interaction of some Grignard reagents with benzophenone, *p*-aminobenzophenone, *p*-dimethylaminobenzophenone, and, of especial interest at this time, *p*,*p*′-tetramethyldiaminobenzophenone or Michler ketone. In each case, the complex formed by a 1:1 ratio of ketone and Grignard reagent regenerated the ketone on hydrolysis. With benzo-

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[1] This is Paper XXX in the series of "Relative reactivities of organometallic compounds; the preceding paper is: THIS JOURNAL, **62**, 980 (1940).

[2] (a) Gilman and Schulze, *ibid.*, **47**, 2002 (1925); (b) *Bull. soc. chim.*, **41**, 1479 (1927); (c) Gilman and Heck, *Rec. trav. chim.*, **48**, 193 (1929); (d) *ibid.*, **49**, 218 (1930); (e) *Ber.*, **62**, 1379 (1929); (f) Gilman, Sweeney and Heck, THIS JOURNAL, **52**, 1604 (1930); (g) Gilman and Heck, *ibid.*, **52**, 4949 (1930).

[3] Werner, *Ann.*, **322**, 296 (1902).

[4] Straus, *ibid.*, **393**, 241 (1912).

[5] Von Braun and Kirschbaum, *Ber.*, **52**, 1725 (1919).

[6] Meisenheimer and Casper, *ibid.*, **54**, 1655 (1921); Meisenheimer, *ibid.*, **61**, 708 (1928); *Ann.*, **442**, 180 (1925); **446**, 76 (1925).

[7] Hess and Rheinboldt, *Ber.*, **54**, 2043 (1921). See, also, Hess and Wustrow, *Ann.*, **437**, 256 (1924).

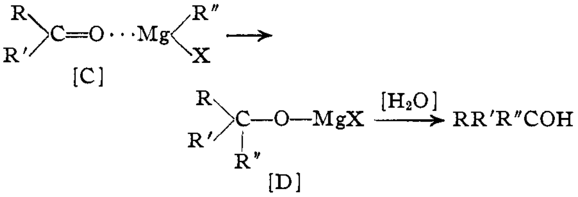
[8] Earlier adaptations of coördinate structures were proposed for the structures of Grignard reagents. Some selected references are: Baeyer and Villiger, *Ber.*, **35**, 1202 (1902); Grignard, *Compt. rend.*, **136**, 1262 (1903); Chelinzeff, *Ber.*, **38**, 3665 (1905). Modern electronic concepts of valence are discussed by Johnson in Chap. 19 of Gilman, "Organic Chemistry," John Wiley and Sons, New York, 1938. See, particularly, p. 1673, for the preliminary coördination and subsequent migrations in the reaction of ketones with Grignard reagents.

[9] Leroide, *Compt. rend.*, **148**, 1611 (1909). Fischer and Hess, *Ber.*, **45**, 912 (1912).

[10] Pfeiffer and Blank, *J. prakt. Chem.*, **152**, 242 (1939).

phenone a 1:2 ratio of ketone to RMgX compound produced intramolecular reaction resulting in the alcohol, triphenylcarbinol. With *p*-aminobenzophenone and *p*-dimethylaminobenzophenone it was found that a ratio of 1:3 of ketone to RMgX compound was necessary to obtain the carbinol under comparable conditions. With Michler ketone, a 1:4 ratio of ketone to RMgX compound gave *p,p'*-tetramethyldiaminodiphenylpropene, $[(CH_3)_2NC_6H_4]_2C{=}CHCH_3$, the dehydration product of the carbinol to be expected from Michler ketone and ethylmagnesium bromide.

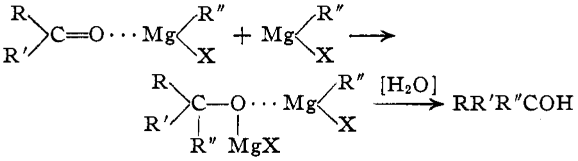
Pfeiffer interpreted the reactions in accordance with his halochrome theory, stating that the unsaturated carbonyl carbon atom in complex [C] can become saturated in two ways. Either the R″ group wanders from the magnesium atom to the carbonyl carbon atom (as Meisenheimer[6] and Hess[7] suggested earlier)



[C]

[D]

or the R″ group of a second Grignard molecule attaches itself to the unsaturated carbon.



In accordance with the observations of Pfeiffer and Blank[10] we find that a complex is formed between Michler ketone and phenylmagnesium bromide in a 1:1 ratio in ether, and that this complex on hydrolysis yields Michler ketone. However, even though the ratio was as low as 1:1, the recovery of ketone was only 88%. Of greater significance is the fact that this mixture gave a color test. One may conclude then that the complexes from Michler ketone and Grignard reagent are not so stable but what they rearrange sufficiently to a true valence type of carbinol salt [D] to give a color test.

The stability of such complexes appears to be influenced by solvents. When the experiment with a 1:1 ratio of Michler ketone to phenylmagnesium bromide was carried out not in ether alone, but in a solution containing mostly benzene, the yield of ketone recovered was only 45%, and there was actually isolated a 42% yield of the carbinol (*p,p'*-tetramethyldiaminotriphenylcarbinol) which is the intermediate compound in the color test for phenylmetallic compounds. From the work mentioned later in this paper on the etherate of triethylgallium, one might expect that compounds like ethers would dampen the reactivity of some organometallic compounds by the formation of coördinate compounds. Fortunately, the color test is always carried out with a benzene solution of Michler ketone and this may help to give the high degree of sensitivity reported[2] for the color tests. In this connection, there is no essential difference in the sensitivity of the color tests for ethylmagnesium bromide and phenylmagnesium bromide.[2c]

Relative Reactivities of Organometallic Compounds.—There appears to be some correlation between the tendency of organometallic compounds to form coördinate compounds with ketones and the relative reactivities of organometallic compounds. We observed no stable complex with Michler ketone, in ether or in benzene, in reactions carried out with phenyllithium at room temperature with equivalent quantities of reactants. The yields of *p,p'*-tetramethyldiaminotriphenylcarbinol were 78% and 92.5%, respectively, and no Michler ketone was recovered. We reported recently[11] that a liberal excess of triphenylgallium was necessary for a color test. This is very probably due to the pronounced tendency of gallium compounds to form complexes. For example, Dennis and Patnode[12] have shown that the simple triethylgallium $[(C_2H_5)_3Ga]$ reacts violently with water; the etherate $[(C_2H_5)_3Ga\cdot(C_2H_5)_2O]$ vigorously; and the ammine $[(C_2H_5)_3Ga\cdot NH_3]$ only very slowly.

With the three arylmetallic compounds mentioned, the order of decrease in relative reactivities and increase in tendency to form coördinate compounds with ketones is: C_6H_5Li, C_6H_5MgBr, $(C_6H_5)_3Ga$.

Relative Reactivities of Functional Groups.—In a study of the relative reactivities of some functional groups with phenylmagnesium bromide, Entemann and Johnson[13] observed that benzophenone and benzoyl chloride were of about the same reactivity. It has been shown that benzoyl chloride is decidedly more reactive than benzophenone when other less reactive or-

[11] Gilman and Jones, THIS JOURNAL, 62, 980 (1940).

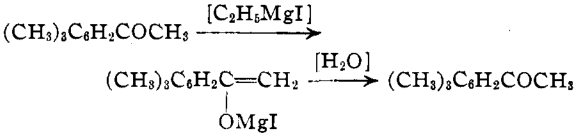
[12] Dennis and Patnode, *ibid.*, 54, 182 (1932).

[13] Entemann and Johnson, *ibid.*, 55, 2900 (1933).

ganometallic compounds like those of mercury,[14a] thallium[14b] and gallium[11] are used. It is quite likely that all organometallic compounds which react with carbonyl containing compounds first form coördinate compounds or complexes of varying stabilities. The less reactive RM compounds may form more stable coördinate linkages with the carbonyl group in ketones than with the carbonyl group in acid halides; and the coördinate complexes with the less reactive RM compounds may stabilize themselves by the direct removal of halogen to form a metal halide rather than by prior addition of the R of the RM compound to the unsaturated carbonyl carbon atom. Varying coördination effects of solvents may influence significantly the relative reactivities of RM compounds.

Steric Hindrance.—It now appears reasonable to suggest that the absence of reaction or very slow reaction observed with some ketones and Grignard reagents may be due appreciably to the formation of coördinate compounds rather than to steric hindrance. Von Braun and coworkers[5,15] observed that $C_6H_5N(CH_3)CH_2CH_2MgX$ reacted with aldehydes but not with ketones; but did find that $C_6H_5N(CH_3)CH_2CH_2CH_2MgX$ reacted with both aldehydes and ketones. These results appear to present an excellent case for steric hindrance for not only is there less steric hindrance with aldehydes than with ketones, but the further removal of the MgX group from the nitrogen in the γ-propyl Grignard reagent should give less steric hindrance than the homologous β-ethyl Grignard reagent. However, not only do aldehydes form less stable complexes than ketones,[6,7] but Heck[2e] showed later that the β-ethyl Grignard reagent did undergo a slower than usual reaction with Michler ketone and color tests were obtained. It is possible that more stable coördination compounds are formed in such cases because of the amino groups present in both the Grignard reagent and the Michler ketone, if one may carry over the analogy from the relatively less reactive ammines of triethylgallium[12] mentioned previously. Furthermore, the experiments of Pfeiffer and Blank[10] illustrate in a striking fashion that the tendency to form coördinate complexes with the Grignard reagent increases progressively with the introduction of amino groups in the ketone: $(C_6H_5)_2CO < (NH_2C_6H_4)(C_6H_5)CO; [(CH_3)_2NC_6H_4](C_6H_5)CO < [(CH_3)_2NC_6H_4]_2CO$.

However, these authors[10] have misinterpreted the experiments of Klages[16] on the reaction of acetomesitylene with ethylmagnesium iodide. These two reactants gave a product which on hydrolysis yielded the original acetomesitylene. The product, however, was not a coördination complex stabilized in some way by steric hindrance, for reaction with the Grignard reagent was not inhibited. Actually, as Kohler and Baltzly[17] have demonstrated, Klages had in hand an iodomagnesium enolate, which on hydrolysis yields the acetomesitylene



$$(CH_3)_3C_6H_2COCH_3 \xrightarrow{[C_2H_5MgI]} (CH_3)_3C_6H_2\underset{\underset{OMgI}{|}}{C}{=}CH_2 \xrightarrow{[H_2O]} (CH_3)_3C_6H_2COCH_3$$

Not only is there no stabilization of a complex with acetomesitylene because of steric hindrance, but an equally sterically hindered Grignard reagent (mesitylmagnesium bromide) gives a strong color test.[2e] Also, color tests are obtained with sterically hindered aliphatic Grignard reagents like the *t*-butylmagnesium halides, *t*-amylmagnesium chloride, and methyldiethylmethylmagnesium chloride.[2b]

Dimorphism with *p,p'*-Tetramethyldiaminotriphenylcarbinol.—Two forms of this carbinol were first reported[18]: a higher melting one from petroleum ether, and a lower melting one from methanol. Later,[19] only the lower melting form was isolated from several solvents including petroleum ether. In our work, we obtained both forms and showed that they could be interchanged by selection of the appropriate solvent.

Experimental Part

Phenylmagnesium Bromide and Michler Ketone.—The Grignard reagent was prepared in a nitrogen atmosphere, and its concentration was determined by the acid-titration procedure.[20]

A 0.5-cc. sample of the 1.06 molar solution of phenylmagnesium bromide was added dropwise to a rapidly stirred suspension of 1.34 g. (0.005 mole) of Michler ketone

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(14) (a) Gilman and Nelson, THIS JOURNAL, **61**, 743 (1939); (b) Gilman and Jones, *ibid.*, **61**, 1513 (1939).

(15) Von Braun, Heider and Müller, *Ber.*, **50**, 1637 (1917).

(16) Klages, *ibid.*, **35**, 2635 (1902).

(17) Kohler and Baltzly, THIS JOURNAL, **54**, 4015 (1932). See subsequent papers in THIS JOURNAL, particularly by Kohler and by Fuson. It would be interesting to learn whether highly reactive organometallic compounds might add to the carbonyl group in compounds like acetomesitylene.

(18) Villiger and Kapetschni, *Ber.*, **45**, 2910 (1912).

(19) Meisenheimer and co-workers, *Ann.*, **423**, 95 (1921).

(20) Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

in 50 cc. of dry ether. The resulting solution gave a strong positive color test when a 1-cc. sample was removed, hydrolyzed and treated with the iodine–acetic acid solution used to complete the color test.[2a] Another 4.5 cc. of the Grignard solution was then added to the Michler ketone suspension, the several operations being carried out in nitrogen, at room temperature, and with rapid stirring. A bright orange precipitate quickly formed as the phenylmagnesium bromide was added. Stirring was continued for fifteen minutes, and then the mixture was hydrolyzed by the addition of 75 cc. of dilute aqueous ammonium chloride solution. The solid which was insoluble in both the ether and water layers was filtered off, washed with ether and water, and shown by the method of mixed melting points to be Michler ketone (1.11 g.). The ether layer was separated and dried, and the ether removed by distillation. The residue was extracted with 20 cc. of hot petroleum ether (b. p. 60–68°) and the insoluble portion (0.08 g.) was shown to be Michler ketone. The total yield of ketone recovered was 1.19 g. or 88%. The experiment was repeated, again using a 1:1 ratio of phenylmagnesium bromide and Michler ketone, and the same results were obtained.

Another reaction was carried out in which 6.8 cc. of 0.73 molar phenylmagnesium bromide solution (0.005 mole of RMgX compound) was added to a stirred solution of 1.34 g. (0.005 mole) of Michler ketone in 40 cc. of dry benzene. A heavy orange precipitate formed quickly, but most of it soon went into solution. After stirring for fifteen minutes at room temperature in an atmosphere of nitrogen, the mixture was hydrolyzed with 75 cc. of dilute ammonium chloride solution. The benzene layer was separated, dried, and then the benzene removed by distillation. The residue was extracted with two 25-cc. portions of hot petroleum ether (b. p. 60–68°). The insoluble portion, after filtering and drying, weighed 0.6 g. and melted between 162 and 165°. After one crystallization from 95% ethanol, the melting point and mixed melting point with an authentic specimen of Michler ketone was 172–173°. The petroleum ether solution deposited, on cooling, 0.72 g. of granular crystals, which after crystallization from methanol melted at 106°, and were shown by the method of mixed melting points to be *p,p'*-tetramethyldiaminotriphenylcarbinol. The yield of recovered Michler ketone was 45% and the yield of carbinol was 42%. This experiment was repeated and the results were practically the same.

Color Tests with Dilute Solutions of Phenylmagnesium Bromide. [A].—A solution of phenylmagnesium bromide was diluted with dry ether and a resulting 0.238 molar solution was used in the following tests. Various quantities of this Grignard solution were added to dry test-tubes containing 2.0-cc. portions of a 0.067 molar benzene solution of Michler ketone. After about one minute, the mixtures were hydrolyzed with 1-cc. portions of water, and then 3 drops of the iodine–glacial acetic acid reagent[2a] were added. The smallest volume of the Grignard solution which would produce a positive color test was 0.07 cc. A good test was obtained when 0.1 cc. was used, and more than 0.2 cc. gave a very strong color test. The ratio of reactants in the case requiring the least quantity of Grignard reagent to give a positive test is 1.7×10^{-5} mole of phenylmagnesium bromide to 1.3×10^{-4} mole of Michler ketone in 2 cc. of solution, or a 13-fold excess of Michler ketone.

[B]. The Grignard solution was again diluted, and this time to a concentration of 0.053 molar. A 5-cc. portion of this solution was required to give a faint positive test with 1 cc. of 0.067 molar Michler ketone solution. The concentrations in this case are equivalent to 8.8×10^{-5} mole of Grignard reagent and 2.2×10^{-5} mole of Michler ketone in 2 cc. of solution, or a four-fold excess of Grignard reagent.

It will be noted that in experiment [A] the relatively high initial ratio of Grignard reagent to ketone together with the presence of much benzene combine to favor a color test. In experiment [B] the situation is reversed for not only is the initial ratio of Grignard reagent to ketone sharply decreased, but the medium is also largely ether.

Phenyllithium and Michler Ketone.—An ether solution of phenyllithium, 0.744 molar in concentration, was prepared in the usual manner from bromobenzene and lithium.[21] To a rapidly stirred suspension of 1.34 g. (0.005 mole) of Michler ketone in 50 cc. of ether was added dropwise 6.8 cc. of the 0.744 molar phenyllithium solution or 0.005 mole of phenyllithium. The suspended material quickly dissolved, and the clear brown solution was stirred at room temperature for fifteen minutes. Hydrolysis was effected by distilled water; the ether layer was separated and dried, and the ether was removed by distillation. The residue was crystallized from petroleum ether, and the white crystalline product weighed 1.35 g. and melted at 121–122°. It was then recrystallized from methanol, and found to melt at 107–107.5°. An authentic sample of *p,p'*-tetramethyldiaminotriphenylcarbinol was obtained by dissolving Merck malachite green in water, precipitating the carbinol with dilute potassium carbonate and crystallizing twice from methanol to give a product melting at 107°. A mixed melting point of the two different samples (one melting at 107–107.5° and the other at 107°) was 107–108°.

The carbinol obtained from phenyllithium (m. p. 107–107.5°) was crystallized twice from petroleum ether (b. p. 60–68°) and again melted at 120°.

No unreacted ketone was recovered, and the yield of carbinol was 78%.

The experiment with phenyllithium was repeated except that benzene was used as the solvent for the ketone. In this case the yield of carbinol melting at 105–107° (mixed melting point) was 1.6 g. or 92.5%. No Michler ketone was recovered.

Summary

A 1:1 mixture of Michler ketone and phenylmagnesium bromide in ether forms a coördination compound, which on hydrolysis gives an 88% recovery of ketone. However, the coördination compound is sufficiently unstable so that there is no interference with the color test for organometallic compounds. The stability of the complex is markedly decreased in an ether–benzene mixture, and in addition to a 45% recovery of ke-

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[21] Gilman, Zoellner and Selby, THIS JOURNAL, 55, 1252 (1933),

tone there was isolated a 42% yield of *p,p'*-tetramethyldiaminotriphenylcarbinol.

A 1:1 mixture of Michler ketone and phenyllithium, in either benzene or ether, forms no stable complex and the only product isolated in excellent yields is the carbinol, which is an intermediate in the color test.

Other aspects of coördination compounds in organometallic chemistry are considered.

AMES, IOWA RECEIVED MARCH 18, 1940

[CONTRIBUTION FROM THE MENDENHALL LABORATORY OF PHYSICS, OHIO STATE UNIVERSITY]

Spectroscopic Evidence for Hydrogen Bonds: The Hexyl Alcohols. I[1]

BY SPENCER C. STANFORD[2] AND WALTER GORDY[3]

Many papers dealing with the infrared absorption spectra of the alcohols have appeared since the discovery that such spectra give direct evidence of the linkage involved in association through hydrogen bonding. The work on the alcohols through 1938 has been summarized by Freymann.[4]

Previous work, pertinent to the present discussion, may be summarized briefly as follows. In the region of the —OH fundamental vibration band, there is found, in the pure liquid at ordinary temperatures, a broad, intense band with its center at 2.95–3.00 μ. On dilution with an inert solvent such as carbon tetrachloride, or on increasing the temperature, the broad band begins to decrease in intensity. Because of this behavior the band is attributed to the presence of associated molecules. As the broad band diminishes in intensity a sharp band appears at 2.75 μ. This band increases in intensity with increased dilution or temperature and is attributed to single alcohol molecules.

Work on the overtones gives results similar to those on the fundamental. However, in the overtone regions, traces of the monomer bands are found, even in the pure liquids at ordinary temperatures, in alcohols above methyl alcohol. The increased symmetry of the potential energy curve of the proton due to hydrogen bonding causes the overtone association bands to be weak in comparison to the fundamental association band, hence the monomer band is not overlapped as much by the association band.[5]

So far as the authors know, no research has been done on a complete series of isomeric alcohols. It appeared of interest to us to study one such series to see if there are detectable differences in association due to variations in structure. Fortunately the hexyl alcohols were available to us, through the courtesy of Dr. Frank Hovorka, of Western Reserve University. The present paper reports the results of the investigation of eight of the seventeen possible hexyl alcohols.

Experimental Technique.—The preparation and purification of hexanol-1, -2, -3, 2-methylpentanol-1, -2, and -4 has been described in the literature.[6] The preparation of 3-methylpentanol-1 and 2-ethylbutanol-1 will be described in publications soon to appear. The boiling point range did not exceed ±0.02° in any of the alcohols studied. The spectrometer and experimental method have been described in a previous paper of this series.[7]

Results and Discussion

The transmission curves for the pure liquids are given in Fig. 1. There is no trace of the monomer band at 2.75 μ. The minimum of the association band is at 2.97 μ for hexanol-1 and 3-methylpentanol-1, the other bands have their minima at 2.95 μ. This slight shift appears to be real, since we were able to reproduce the position of the minima.

There is a gradual increase in the per cent. transmission at the minimum and a decrease in the breadth of the band as one goes from hexanol-1 to hexanol-3. These and differences in intensity among the other pure liquid curves could possibly be due to error in reproducing cell thickness with such thin cells. It is probable, however, that

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(1) A summary of this paper was read at the Ohio-Michigan Regional Meeting of the American Chemical Society, East Lansing, Michigan, October 28, 1939.

(2) Department of Chemistry, College of Wooster, Wooster, Ohio.

(3) Department of Physics, Mary Hardin-Baylor College, Belton, Texas.

(4) Freymann, *J. phys. radium*, **9**, 517 (1938).

(5) See, for example; Errera and Sack; *Trans. Faraday Soc.*, **34**, 728 (1938).

(6) (a) Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933); (b) Hovorka, Lankelma and Stanford, *ibid.*, **60**, 820 (1938).

(7) Gordy and Stanford, *ibid.*, **62**, 497 (1940).